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Synthesis of poly(pyridylthioether) dendrimers incorporating a $Fe_2(CO)_6$ cluster core

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Abstract—New pyridylthioether-based dendrons bearing a thiol moiety at their focal point have been prepared by a convergent synthetic approach. These dendrons were readily attached to a $Fe_2(CO)_6$ core to generate two-directional dendritic molecules incorporating an iron-carbonyl cluster.

1. Introduction

Organic–inorganic composites deriving from the encapsulation of metal clusters within dendrimer molecules are emerging as a new class of nanosized materials that are expected to have applications in many areas including catalysis,[1] molecular recognition,[2] and photoactive device engineering.[3] In these materials, the chemical interaction between an organic array and the inorganic counterpart can be either covalent or noncovalent. The noncovalent method of incorporation, which uses dendrimers as both nanoreactor that sequesters metal ions and stabilizer, leads to dendrimer-encapsulated metal nanoclusters. Moreover, the size of such metallic nanoparticles can be controlled by the size of the dendrimer template.[4] Typically, the synthetic strategy to achieve encapsulation relies on complexation of metal ions into the dendrimer interior and their subsequent chemical reduction to zero-valent form. Most syntheses of these nanocomposites concern noble metals[1,4–7] but dendrimers incorporating copper[8] have also been reported. Recently, Fréchet-type dendritic wedges[9] focally functionalized with a metal-coordinating group, such as a thiol[10] or 4-pyridone[11] moiety, were assembled around gold clusters affording dendron-stabilized gold nanoparticles in which the average size of the metallic nanoparticles seems to be correlated to the generation number of the dendritic wedges.

The covalent encapsulation of a metal cluster inside dendritic architectures was first reported by Gorman and co-workers who prepared metallodendrimers containing a $[Fe_4S_4]^{2+}$ cluster core unit via replacement of bulky aliphatic thiols at the four vertices of this cluster by dendron-functionalized aromatic thiols.[12] The main object of Gorman's research group, however, was to understand the relationship between dendritic structure and electrochemical properties of encapsulated iron–sulfur clusters.[13]

Because dendritic wedges bearing a thiol functionality at their focal point play a key role in the chemistry of both noncovalent and covalent dendrimer-encapsulated metal clusters we decided to explore the synthesis of a new series of thiol-functionalized pyridylthioether-based dendrons.

There are two features of our dendrons that make them appealing as precursors of dendron-functionalized inorganic clusters. First, the S–N–S terdentate ligands constituting the dendritic framework are potential binding sites of transition metals.[14] This, therefore, may enable the preparation of heterometallic dendritic assemblies. Second, the pyridylthioether-based repeating units are directly connected through phenyl groups affording a scaffold that could facilitate the electron transfer between dendron units and a focal point.

A prerequisite to successfully achieve the covalent encapsulation of transition-metal clusters using these types of focally-functionalized dendrons, is an efficient synthetic methodology that provides easy access to products of high purity.

To accomplish such a task we have chosen to investigate the chemistry of the dinuclear hexacarbonyls of formula $[Fe_2(CO)_6(SR)_2]$. It has been previously shown that the

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reactions between $Fe_3(CO)_{12}$ and bulky aromatic thiols afford compounds of the type $[Fe_2(CO)_6(\mu\text{-}SR)_2]$ in good yields.[15]

We focused our efforts on the preparation of analogous systems with dendritic topologies. The results of the synthetic studies which allowed us to assembly novel pyridyl thioether dendrons around an iron-carbonyl core are presented here.

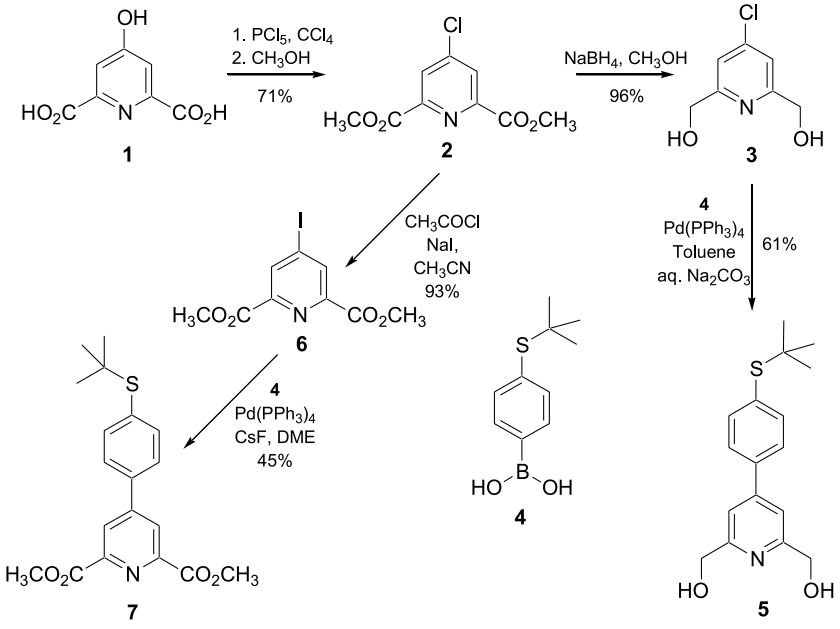
2. Results and discussion

The synthetic route we have adopted to prepare a dendrimer-encapsulated $Fe_2(CO)_6$ core unit consists of treating commercially available $Fe_3(CO)_{12}$ with a dendron-functionalized aromatic thiol which was synthesized via convergent methodology.[9] The building block designed for the synthesis of all dendron generations, namely compound **12**, is depicted in Scheme 2, along with the synthetic approach we have developed for its preparation.

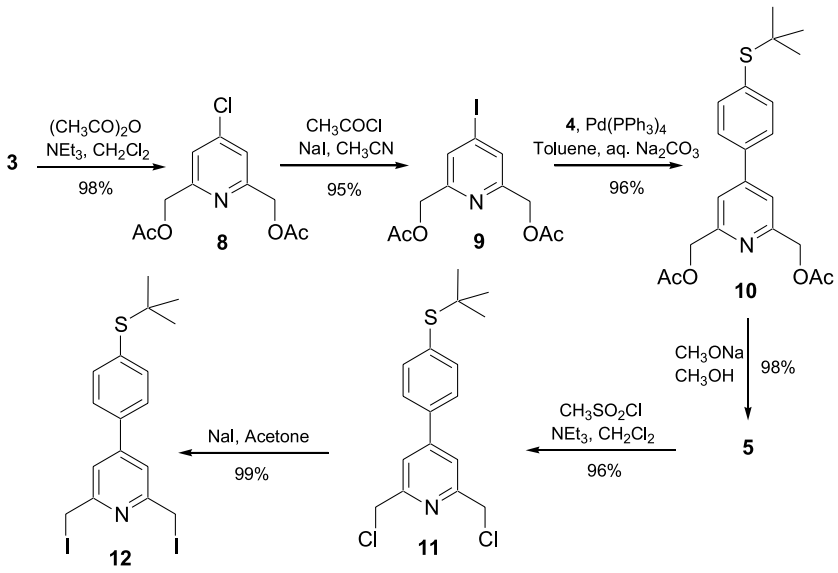
The synthesis of **12** was initiated from the commercial diacid **1**, (Scheme 1) which was converted to dimethyl 4-chloropyridine-2,6-dicarboxylate **2** in 71% yield according to suitably modified literature procedures.[16] Subsequent reduction of the ester functionalities to alcohols, using $NaBH_4$ in methanol,[17] afforded diol **3** in 96% yield. Halopyridine **3** was then treated with boronic acid **4**, prepared[18] in high yield and purity from 4-bromobenzenethiol, employing the Suzuki cross-coupling conditions (toluene/H_2O, Na_2CO_3, $Pd(PPh_3)_4$) to give the aryl-substituted pyridine derivative **5** in 61% yield after chromatographic purification. Although we have obtained the desired compound **5** in reasonable yield, the purification step was arduous because of the difficulty in separating **5** from the starting materials. To overcome this problem and to improve the yield of cross-coupling product an alternative approach to **5** was explored.

Since the order of reactivity of the aryl halides towards oxidative addition to a Pd(0) complex suggests that iodopyridines are much more effective substrates than the corresponding chloropyridines, the chloro-substituted pyridine **2** was converted to the corresponding iodo derivative **6** in 93% yield by sonochemical reaction with acetyl chloride, and NaI in dry CH_3CN.[19] Unfortunately, the coupling reaction of **6** with boronic acid **4** under anhydrous conditions in the presence of CsF as base[20] only afforded **7** in moderate yield (40–60%). However, the yields compare well with those reported by Lohse,[21] who investigated the reactivity of methyl 4-chloropyridine-2-carboxylate in a Suzuki reaction. These relatively low yields, presumably due to the sensitivity to base of the esters functions, prompted us to pursue the preparation of **5** from diol **3** by a four-step procedure that proved to give superior results regarding achievable yield of compound **5**.

Thus, as outlined in Scheme 2, the hydroxyl functions of **3** were acylated with Ac_2O and trietylamine to afford the corresponding acetate **8** in essentially quantitative yield. To increase the reactivity of **8** in cross-coupling reactions the chloro group of this compound was replaced by iodo employing *trans*-halogenation conditions (AcCl/NaI, CH_3CN, room temperature, ultrasonic irradiation) to produce compound **9** in 95% yield. As expected, halopyridine **9** furnished the arylpyridine **10** in excellent yield (96%) by a Suzuki reaction using boronic acid **4** as coupling partner of **9**, $Pd(PPh_3)_4$ as catalyst, $NaHCO_3$ as base, and toluene/H_2O as solvent system. Due to the acetyl groups protecting the hydroxyl moieties, the solubility of **10** in organic solvents was significantly enhanced relative to the unprotected derivative allowing easy separation and purification by silica gel chromatography of this material after reaction. Furthermore, the acetate moiety can be selectively and cleanly removed under mild basic conditions. Accordingly, deacetylation of compound **10** by alkaline methanolysis generated the diol **5**, as formed by Suzuki coupling of **3** with **4**, in 98% yield (88% overall yield from **3**).



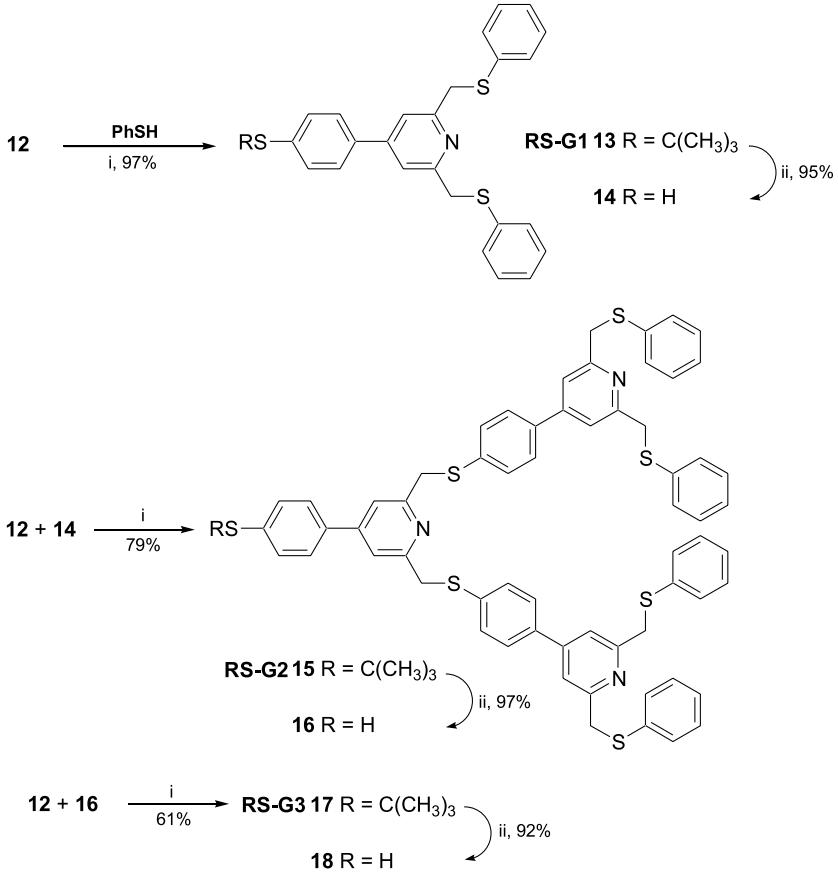
Scheme 1. Synthesis of the intermediates **5** and **7**.



Scheme 2. Synthesis of the building block **12**.

Reaction of **5** with methanesulfonyl chloride and triethylamine furnished the corresponding chloride **11** in 96% yield, which was subsequently converted into its iodo analogue **12** in 99% yield by reaction with NaI in acetone because iodides easily undergo a nucleophilic substitution. On the contrary, direct conversion of diol **5** to diiodide **12** by I_2/imidazole/PPh_3[22] gave poor yields.

The reactivity of the pyridine-based building block **12** evidently emerges in the synthesis of the first-generation dendron. As a matter of fact, coupling diiodide **12** with slightly over 2 equiv of thiophenol under standard etherification conditions (DMF/K_2CO_3) proceeded quickly (2 h, room temperature) to give the protected first-generation dendron **13** in 97% yield (Scheme 3).



Scheme 3. Synthesis of dendrons: (i) DMF/K_2CO_3, rt; (ii) thioanisole, TFA, CF_3SO_3H, rt.

It is well-known that some *S*-thiophenol protecting groups, such as thioethers, are particularly stable and their selective removal may be difficult to accomplish in high yield.[23] Nevertheless, the *tert*-butyl moiety in compound **13** could be easily removed using the thioanisole-trifluoromethanesulfonic acid (TFMSA)-trifluoroacetic acid system[24] to produce the desired thiol-funtionalized dendron **14** in 95% yield. In accordance with a convergent growth strategy thiol **14** was then reacted with diiodide **12**, under conditions similar to those used for **13**, to give the second-generation dendron **15** (79%), which was deprotected to the corresponding thiol **16** in 97% yield by reacting with thioanisole-trifluoromethanesulfonic acid (TFMSA)-TFA at room temperature for 4 h (Scheme 3). While the deprotection proceeds smoothly, the purification of the crude product of this reaction by silica gel chromatography proved to be unsuitable affording the thione form of **16** (Chart 1), as confirmed by NMR and mass spectrometry analysis. Thus to circumvent this problem, the thiol **16** was purified by repeated precipitation from dichloromethane–hexane mixtures.

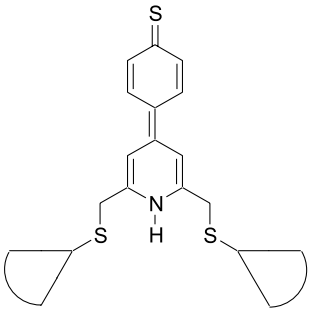


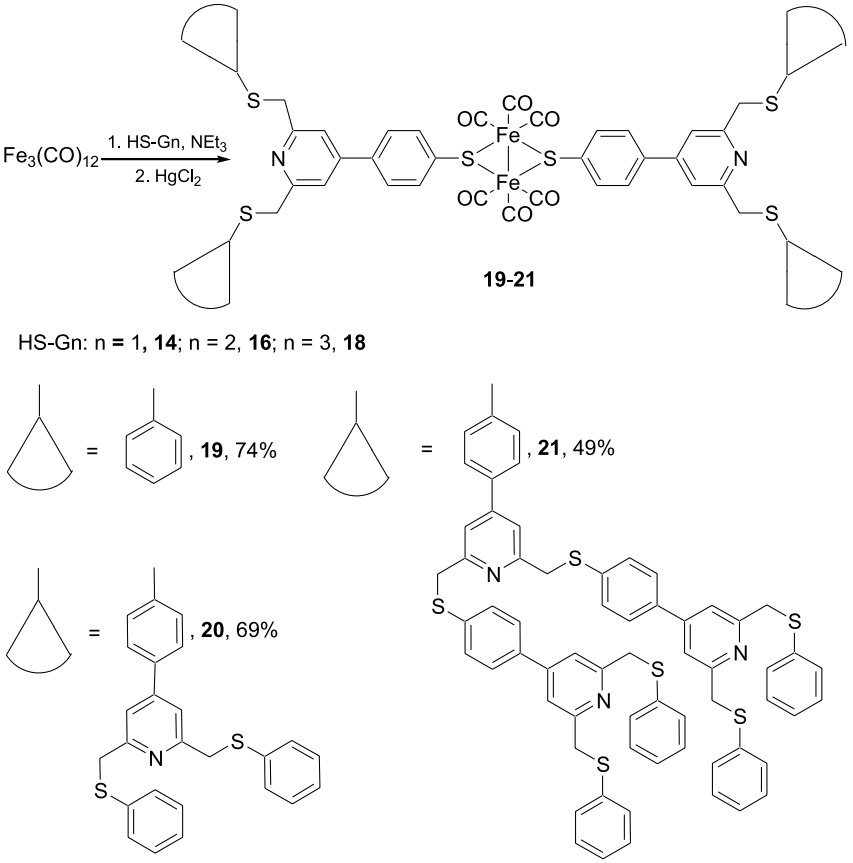
Chart 1. Thione form of pyridylthioether-based dendrons focally functionalized with a thiol unit.

The third-generation dendritic wedge **17** was prepared in a similar way to its earlier generation analogue. However, the coupling of **12** with thiol **16** gives **17** in moderate yields (61%), presumably due both to steric problems and the inherent low stability of the thiol moiety. Following the same procedure that gave compounds **14** and **16**, dendron **17** was deprotected to furnish the corresponding thiol derivative **18** in 92% yield.

All dendrons display NMR spectra consistent with their structures. The aliphatic regions in the ^{1}H NMR spectra provide the most important information since the aliphatic protons give well-resolved signals. The number of singlets at around 4.25–4.36 ppm due to CH_2S protons clearly corresponds with the generation of the dendron involved. Moreover, the relative integrations for these signals and the aromatic proton signals match perfectly with the proposed structures.

Finally, the conversion from *tert*-butyl protected dendron to the corresponding thiol derivative was easily confirmed by the complete absence of the signal associated with the *tert*-butyl moiety coupled with the presence of a new resonance at 3.52–3.55 ppm for the SH group.

The last step of our approach involved the assembly of the



Scheme 4. Synthesis of dendrimers with $Fe_2(CO)_6$ as core.

synthesized dendrons around a transition-metal cluster. To this end we initially reacted $Fe_3(CO)_{12}$ with thiol **14** in THF, using triethylamine as a base, followed by treatment with $HgCl_2$ in a one-pot procedure (Scheme 4), which has been suggested from the communication describing the reactions of alkyl- and arylmercuric halides with $[Et_3NH][((-CO)-((-RS)Fe_2(CO)_6]$ complexes.[25] According to the above procedure, the desired cluster compound **19** was obtained in 74% yield after chromatographic purification. The analogous reaction of $Fe_3(CO)_{12}$ with dendron-functionalized thiols **16** and **18** afforded the iron cluster dendrimers **20** and **21** in 69 and 49% yield, respectively (Scheme 4).

The formation of metallodendrimers **19–21** was confirmed by disappearance of the thiol signal in their ^1H NMR spectra. The ^1H NMR spectrum of the third generation dendrimer **21** in $CDCl_3$ was broad and structureless, probably as a consequence of restricted movement of the attached dendrons, but consistent with the proposed structure in DMSO-d6 at 50 °C. However, the structure of **21** could be established unambiguously by ^{13}C NMR that showed the expected resonances for the aliphatic and aromatic carbons of the dendritic building block as well as the signal for the carbonyl groups of the cluster core. Further evidence for the formation of **19–21** was provided by their IR spectra that showed in the carbonyl region the expected absorbances for complexes of this type.[15] To confirm the molecular masses of the synthesized metallodendrimers, the MALDI-TOF technique was applied. Unfortunately, MALDI-TOF mass spectra of molecules **19–21** did not show the expected molecular ion peaks, but instead signals corresponding to the mass of the starting dendron were observed. Therefore these results indicate that the structure of the iron-carbonyl core dendrimers is too weak to withstand the conditions of the MALDI-TOF analysis.

Electrospray ionization technique was also used as an alternative mass analysis in an attempt to provide characterization of the dendritic complexes. However, these attempts were unsuccessful.

Though the mass spectrometric studies did not provide straightforward evidence for the formation of **19–21**, the elemental analysis data coupled with the NMR and IR spectra offered clear indication that the desired compounds had been successfully obtained.

3. Conclusions

Following a convergent strategy a series of novel pyridylthioether dendrimers that incorporate a $Fe_2(CO)_6$ unit in the core have been assembled by coupling commercially available triiron dodecacarbonyl with synthetic monodendrons. These dendrons have been constructed by employing the activated and protected building block 4-[4-*tert*-butylthio(phenyl)]-2,6-bis(iodomethyl)pyridine (**12**) which has been efficiently generated by a multistep sequence. The key dendron growth steps involved coupling via Williamson reaction conditions followed by deprotection of the thiol function. The formation of the novel metallodendrimers is supported by ^1H, ^{13}C, and FT-IR spectroscopy, and elemental analyses.

Preliminary experiments confirm that these metal cluster core dendrimers are capable of binding the same number of palladium atoms as the tridentate SNS units affording a metallodendrimer that incorporates two kinds of transition metal centres in its structure. The preparation and investigation of these complexes are currently underway. We are also investigating the electrochemical properties of these dendritic systems to gain insight into structure-property relationships.

4. Experimental

4.1. General comments

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately before use. Methanol and acetone were dried and stored over 3 and 4 Å molecular sieves, respectively. *N*,*N*-Dimethylformamide (DMF), dichloromethane, acetonitrile and triethylamine were distilled from calcium hydride. Other solvents and reagents were used as received. Flash chromatography was performed on 230–400 mesh silica gel (Macherey–Nagel). ^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions, unless otherwise indicated, on a Bruker Avance 300 spectrometer using the solvent signal as internal standard. IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer. Melting points were taken in capillary tubes with a Buchi 535 apparatus and are uncorrected.

Mass spectra of dendrimers were obtained by Matrix Assisted Laser Desorption Ionisation Mass Spectrometry (MALDI-MS), using a Voyager-DE PRO instrument (Applied Biosystems, Foster City, CA, USA), operating in positive linear mode. The instrumental conditions were: acceleration voltage: 20 keV; grid voltage = 93%; guide wire = 0.3%; delay time = 200 ns. The matrix used was (2-(*p*-hydroxy-phenylazo)benzoic acid (HABA), at a concentration of 10 mg/mL in choloroform. 0.5 mg of dendrimer was dissolved in 1 mL of $CHCl_3$ and 5 μL of this solution were added to the same volume of the matrix solution. About 1 μL of the resulting solution was deposited on the stainless steel sample holder and allowed to dry before introduction into the mass spectrometer.

ESI mass spectra were obtained using an LCQ (Finnigan, Palo Alto, CA, USA), operating in positive ion modes. The entrance capillary temperature was 270 °C and the capillary voltage was kept at +3 kV. Sample solutions (at a concentration of about 5×10^{-6} M in $CHCl_3$) were introduced by direct infusion at a flow rate of 8 μL/min. The He pressure inside the trap was kept constant. The pressure directly read by ion gauge (in the absence of the N_2 stream) was 2.8×10^{-5} Torr.

4.1.1. Dimethyl 4-chloropyridine-2,6-dicarboxylate (2). A mixture of anhydrous 4-hydroxypyridine-2,6-dicarboxylic acid (64.45 g, 0.32 mol) and PCl_5 (200.2 g, 0.96 mol) in CCl_4 (300 mL) was heated under reflux for 4 h. Then dry methanol (200 mL) was added dropwise over a period of 40 min, and the resulting mixture was heated under reflux for 1 h. The solvent was evaporated to afford a tan yellow solid which was dissolved in water (500 mL) and

neutralized with Na_2CO_3. The resulting solid was collected by filtration, washed with water and dissolved in $CHCl_3$ (400 mL). The organic solution was washed with saturated aqueous Na_2CO_3 (3×200 mL), brine (200 mL), and dried over $MgSO_4$. Removal of the solvent under reduced pressure and recrystallization of the residue from methanol gave **2** as white crystals (52.6 g, 71%). Mp 139–140 °C. IR (KBr), ν: 1722, 1710, 1578 cm^{-1}. ^1H NMR: δ 4.02 (s, 6H, CH_3), 8.29 (s, 2H, PyH). ^{13}C NMR: δ 53.9 (CH_3), 128.7 (3,5-PyC), 147.2 (4-PyC), 149.8 (2,6-PyC), 164.5 (CO). Anal. calcd for $C_9H_8ClNO_4$ (229.6): C, 47.08; H, 3.51;Cl, 15.44; N, 6.10. Found: C, 46.85; H, 3.44;Cl, 15.70; N, 6.00.

4.1.2. 4-Chloro-2,6-bis(hydroxymethyl)pyridine (3). This compound was prepared from **2** following a literature procedure[17] in 96% yield.

4.1.3. 4-[4-*tert*-Butylthio(phenyl)]-2,6-bis(hydroxymethyl)pyridine (5). *Method A.* A stirred mixture of diol **3** (1.00 g, 5.76 mmol), 4-(*tert*-butylthio)phenylboronic acid **4** (2.42 g, 11.52 mmol), $Pd(PPh_3)_4$ (1.33 g, 1.52 mmol) in toluene (100 mL) and saturated aqueous Na_2CO_3 (50 mL) was heated under reflux under argon for 64 h. After cooling to room temperature the reaction mixture was extracted with ethyl acetate (3×50 mL) and the combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography on silica gel eluting with 5–10% methanol in $CHCl_3$. Removal of the solvent followed by precipitation of the residue from CH_2Cl_2/hexane gave **5** as a white solid (1.07 g, 61%).

Method B. A stirred solution of **10** (4.00 g, 10.32 mmol) and CH_3ONa (4.13 mmol, from 94 mg of Na) in dry methanol (50 mL) was heated under reflux under argon for 4 h. Then the reaction mixture was evaporated to dryness and the residue taken up in CH_2Cl_2 (150 mL). The resulting organic solution was washed with water (2×50 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was precipitated from CH_2Cl_2/hexane to afford **5** as a white solid (3.08 g, 98%). Mp 119–120 °C. IR (KBr), ν: 1610 cm^{-1}. ^1H NMR (DMSO-d6): δ 1.29 (s, 9H, *t*-Bu) 4.59 (d, 4H, J=5.9 Hz, CH_2), 5.44 (d, 2H, J=5.9 Hz, OH), 7.62 (s, 2H, PyH), 7.65 (d, 2H, J=8.5 Hz, 3PhH), 7.78 (d, 2H, J=8.5 Hz, 2-PhH). ^{13}C NMR (DMSO-d6): δ 31.1 (C(CH_3)$_3$), 46.5 (C(CH_3)$_3$), 64.5 (CH_2), 116.0 (3,5-PyC), 127.4 (2-PhC) 133.6 (4-PhC), 137.9 (3-PhC), 138.7 (1-PhC), 147.6 (4-PyC), 162.3 (2,6-PyC). Anal. calcd for $C_{17}H_{21}NO_2S$ (303.4): C, 67.29; H, 6.98; N, 4.62. Found: C, 67.32; H, 6.81; N, 4.49. ESI/MS *m/z*: 304 $[M+H]^+$ (Rel. Int.=100%).

4.1.4. Dimethyl 4-iodopyridine-2,6-dicarboxylate (6). Acetyl chloride (5.15 g, 65.61 mmol) was added to a mixture of chloropyridine **2** (5.00 g, 21.77 mmol) and NaI (65.28 g, 435.5 mmol) in dry CH_3CN (150 mL) at 0 °C. The reaction mixture was sonicated for 5 h under an argon atmosphere maintaining the bath temperature below 50 °C. After cooling to 0 °C saturated aqueous Na_2CO_3 (75 mL) and CH_2Cl_2 (150 mL) were added. The organic layer was washed with saturated aqueous $Na_2S_2O_3$ (100 mL), water (2×100 mL), and dried over $MgSO_4$. Removal of the solvent under reduced pressure and recrystallization of the residue from methanol gave **6** as a white solid (6.51 g, 93%). Mp 174–175 °C. IR (KBr) ν: 1751, 1558 cm^{-1}. ^1H NMR: δ 4.03 (s, 6H, CH_3), 8.67 (s, 2H, PyH). ^{13}C NMR: δ 53.3 (CH_3), 106.9 (4-PyC), 137.0 (3,5-PyC), 148.2 (2,6-PyC), 163.8 (CO). Anal. calcd for $C_9H_8INO_4$ (321.1): C, 33.67; H, 2.51; N, 4.36. Found: C, 33.72; H, 2.66; N, 4.38.

4.1.5. Dimethyl 4-[4-*tert*-butylthio(phenyl)]pyridine-2,6-dicarboxylate (7). A solution of **6** (500 mg, 1.56 mmol), 4-(*tert*-butylthio)phenylboronic acid **4** (393 mg, 1.87 mmol), CsF (473 mg, 3.12 mmol) and $Pd(PPh_3)_4$ (90 mg, 0.078 mmol) in dry DME (10 mL) was stirred under argon at 60 °C for 18 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (2×25 mL). The combined organic extracts were washed with water (2×50 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue subjected to flash chromatography on silica gel eluting with CH_2Cl_2/ethyl acetate 4:1. Removal of the solvent followed by precipitation of the residue from CH_2Cl_2/hexane gave **7** as a yellowish solid (251 mg, 45%). Mp 139–140 °C. IR, ν: 1741, 1716, 1603 cm^{-1}. ^1H NMR: δ, 1.34 (s, 9H, *t*-Bu) 4.06 (s, 6H, CH_3), 7.67–7.74 (m, 4H, PhH), 8.55 (s, 2H. PyH). ^{13}C NMR: δ 31.0 (C(CH_3)$_3$), 46.7 (C(CH_3)$_3$), 53.3 (CH_3), 125.6 (3,5-PyC), 127.1 (2-PhC), 135.8 (1-PhC), 136.3 (4-PyC), 138.1 (3-PhC), 148.9 (4-PhC), 150.4 (2,6-PyC), 165.2 (CO). Anal. calcd for $C_{19}H_{21}NO_4S$ (359.44): C, 63.49; H, 5.98; N, 3.90. Found: C, 63.66; H, 5.91; N, 4.05.

4.1.6. 4-Chloro-2,6-bis(acetoxymethyl)pyridine (8). To a stirred solution of **3** (5.00 g, 28.8 mmol) in dry CH_2Cl_2 (150 mL) and dry triethylamine (13.11 g, 129.6 mmol) was added acetic anhydride (11.76 g, 115.21 mmol). The reaction mixture was heated under reflux under argon for 2 h and then cooled to room temperature. CH_2Cl_2 (100 mL) was added, and the resulting solution was washed with saturated aqueous $NaHCO_3$ (50 mL), water (2×50 mL), and dried over $MgSO_4$. After filtration, the solvent was removed from the filtrate and the pure product (7.24 g, 98%) was obtained as a white solid. Mp 50–51 °C. IR (KBr), ν: 1732, 1578 cm^{-1}. ^1H NMR: δ 2.19 (s, 6H, CH_3), 5.20 (s, 4H, CH_2), 7.30 (s, 2H, PyH). ^{13}C NMR: δ, 20.7 (CH_3), 65.9 (CH_2), 120.7 (3-PyC), 145.5 (4-PyC), 157.3 (2-PyC), 170.2 (CO). Anal. calcd for $C_{11}H_{12}ClNO_4$ (257.7): C, 51.27; H, 4.69; N, 5.44. Found: C, 51.46; H, 4.84; N, 5.42.

4.1.7. 4-Iodo-2,6-bis(acetoxymethyl)pyridine (9). This compound was prepared analogously to **6** by reacting **8** (4.45 g, 17.29 mmol), acetyl chloride (4.07 g, 51.87 mmol), and NaI (18.14 g, 121.03 mmol) in dry CH_3CN (90 mL), except the reaction mixture was sonicated for 18 h instead of 5 h while the bath temperature was allowed to warm to 65 °C. After workup, the crude product was purified by precipitation from CH_2Cl_2/hexane to give **9** as a pale yellow solid (5.73 g, 95%). Mp 116–117 °C. IR (KBr), ν: 1751, 1558 cm^{-1}. ^1H NMR: δ 2.18 (s, 6H, CH_3), 5.15 (s, 4H, CH_2), 7.66 (s, 2H, PyH). ^{13}C NMR: δ 20.8 (CH_3), 65.7 (CH_2), 106.7 (4-PyC), 129.7 (3,5-PyC), 156.4 (2,6-PyC), 170.3 (CO). Anal. calcd for $C_{11}H_{12}INO_4$ (349.12): C, 37.84; H, 3.46; N, 4.01. Found: C, 37.95; H, 3.49; N, 4.19.

4.1.8. 4-[4-*tert*-Butylthio(phenyl)]-2,6-bis(acetoxymethyl)pyridine (10). A mixture of boronic-acid **4**

(2.65 g, 12.6 mmol), **9** (4.00 g, 11.46 mmol), $Pd(PPh_3)_4$ (264 mg, 0.229 mmol) in toluene (90 mL) and saturated aqueous $NaHCO_3$ (75 mL) was stirred under argon at 50 °C for 72 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×50 mL) and the combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2/ethyl acetate 4:1. Removal of the solvent followed by recrystallization of the residue from methanol gave **10** as a white solid (4.25 g, 96%). Mp 157–158 °C. IR (KBr), *ν*: 1745, 1736, 1610 cm^{-1}. ^1H NMR: *δ*, 1.29 (s, 9H *t*-Bu) 4.59 (s, 4H, CH_2), 7.62 (s, 2H, PyH), 7.65 (d, *J*=8.5 Hz, 2H, 3-PhH), 7.78 (d, *J*=8.5 Hz, 2H, 2-PhH). ^{13}C NMR: *δ*, 20.9 (CH_3), 31.0 (C(*C*H_3)$_3$), 46.4 (*C*(CH_3)$_3$), 66.8 (CH_2), 119.0 (3,5-PyC), 127.1 (3-PhC), 134.5 (1-PhC), 137.9 (2-PhC), 138.1 (4-PyC), 149.5 (4-PhC), 156.3 (2,6-PyC), 170.6 (CO). Anal. calcd for $C_{21}H_{25}NO_4S$ (387.49): C, 65.09; H, 6.50; N, 3.61. Found: C, 65.11; H, 6.48; N, 3.42.

4.1.9. 4-[4-*tert*-Butylthio(phenyl)]-2,6-bis(cloromethyl)-pyridine (11). Methanesulfonyl chloride (8.49 g, 74.15 mmol) was slowly added over 10 min to a cooled solution (0 °C) of **5** (7.50 g, 24.72 mmol) in dry CH_2Cl_2 (100 mL) containing triethylamine (8.0 g, 79.1 mmol) under argon. The mixture was stirred at room temperature for 2 h, then was heated to reflux for 14 h and, after cooling to room temperature, CH_2Cl_2 (100 mL) and saturated aqueous $NaHCO_3$ (100 mL) were added. The organic layer was washed with water, dried over $MgSO_4$ and filtered. The filtrate was passed through a silica plug eluting with CH_2Cl_2. Removal of the solvent under reduced pressure gave **11** as a pale brown solid (8.10 g, 96%). Mp 82–83 °C. IR (KBr), *ν* 1605 cm^{-1}. ^1H NMR: *δ*, 1.35 (s, 9H *t*-Bu) 4.74 (s, 4H, CH_2), 7.64 (d, *J*=8.6 Hz, 2H, 2-PhH), 7.67 (s, 2H, PyH), 7.68 (d, *J*=8.6 Hz, 2H, 2-PhC). ^{13}C NMR: *δ* 31.4 (C(*C*H_3)$_3$), 46.9 (*C*(CH_3)$_3$), 46.9 (CH_2), 120.4 (3,5-PyC), 127.5 (2-PhC), 135.2 (4-PhC), 138.1 (1-PhC), 138.4 (3-PhC), 150.5 (4-PyC), 157.4 (2,6-PyC). Anal. calcd for $C_{17}H_{19}Cl_2NS$ (340.31): C, 60.00; H, 5.63; N, 4.12. Found: C, 59.81; H, 5.58; N, 4.26.

4.1.10. 4-[4-*tert*-Butylthio(phenyl)]-2,6-bis(iodomethyl)-pyridine (12). A stirred solution of **11** (3.02 g, 8.86 mmol) and NaI (6.64 g, 44.31 mmol) in dry acetone (50 mL) was heated under reflux under argon for 2 h. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (100 mL). The organic solution was washed with saturated aqueous $Na_2S_2O_3$ (100 mL), water and dried over $MgSO_4$. The mixture was filtered and the solvent was removed from the filtrate affording **12** as a pale yellow solid (4.58 g, 99%). Mp 155 °C Dec. IR (KBr), *ν*: 1603 cm^{-1}. ^1H NMR: *δ*, 1.34 (s, 9H, *t*-Bu) 4.56 (s, 4H, CH_2), 7.49 (s, 2H, PyH) 7.59 (d, *J*=8.5 Hz, 2H, 2-PhH), 7.66 (d, *J*=8.5 Hz, 2H, 3-PhH). ^{13}C NMR: *δ* 5.7 (CH_2), 30.9 (C(*C*H_3)$_3$), 46.4 (*C*(CH_3)$_3$), 119.7 (3,5-PyC), 126.9 (2-PhC), 134.6 (4-PhC), 137.5 (1-PhC), 137.9 (3-PhC), 149.7 (4-PyC), 158.8 (2,6-PyC). Anal. calcd for $C_{17}H_{19}I_2NS$ (523.21): C, 39.02; H, 3.66; N, 2.68. Found: C, 39.11; H, 3.61; N, 2.83. ESI/MS *m/z*: 524 $[M+H]^+$ (Rel. Int.=100%).

4.1.11. *tert*-BuS-G1 (13). To a stirred suspension of anhydrous K_2CO_3 (2.19 g, 15.86 mmol) and benzenethiol (1.33 ml, 13.01 mmol) in dry DMF (30 mL) was added **12** (3.32 g, 6.34 mmol) portionwise over 10 min. The resulting mixture was stirred at room temperature under an argon atmosphere for 2 h and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (100 mL) and the organic extract was washed with saturated aqueous Na_2CO_3 (50 mL), water (2×50 mL), and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the resulting crude product was recrystallized from methanol to give **13** as a white solid (2.98 g, 97%). Mp 54–55 °C. IR (KBr), *ν*: 1599 cm^{-1}. ^1H NMR: *δ*, 1.33 (s, 9H, *t*-Bu), 4.31 (s, 4H, CH_2), 7.22 (tt, 2H, *J*=7.1, 1.4 Hz, CH_2S-Ph*H*), 7.27 (tt, 4H, *J*=7.3, 1.4 Hz, CH_2S-Ph*H*), 7.37 (dd, 4H, *J*=8.0, 1.5 Hz, CH_2S-PhH), 7.37 (s, 2H, PyH), 7.41 (d, 2H, *J*=8.3 Hz, 2-PhH), 7.59 (d, 2H, *J*=8.3 Hz, 3-PhH). ^{13}C NMR: *δ*, 31.4 (C(*C*H_3)$_3$), 41.0 (CH_2), 46.8 (*C*(CH_3)$_3$), 119.7 (3,5-PyC), 126.8, 127.4, 129.3, 130.3, 134.5, 136.2, 138.2, and 138.6 (PhC), 149.2 (4-PyC), 158.4 (2,6-PyC). MALDI-TOF MS *m/z*: 488 $[M+H]^+$; calcd for $C_{29}H_{30}NS_3$: 488.7.

4.1.12. HS-G1 (14). To a stirred solution of **13** (4.22 g, 8.64 mmol) in thioanisole (20 mL) was slowly added trifluoroacetic acid (2.9 mL, 38.9 mmol) and triflic acid (2.7 mL, 30.25 mmol). The resulting mixture was kept stirring at room temperature under an argon atmosphere for 4 h and then CH_2Cl_2 (100 mL) was added. The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL), water (2×50 mL), and dried over $MgSO_4$. After filtration, the organic phase was evaporated to dryness and the residue was purified by repeated precipitation from CH_2Cl_2/hexane to give **14** as a yellow solid (354 g, 95%). Mp 110–110.5 °C. IR (KBr) *ν*: 1605 cm^{-1}. ^1H NMR: *δ*, 3.54 (s, 1H, SH), 4.30 (s, 4H, CH_2), 7.19 (tt, 2H, *J*=7.0, 1.5 Hz, CH_2S-Ph*H*), 7.26 (btt, 4H, *J*=7.5, 1.5 Hz, CH_2S-Ph*H*), 7.33-7.31 (m, 4H, CH_2S-Ph*H*), 7.32 (s, 2H, PyH), 7.34–7.83 (m, 4H, PhH). ^{13}C NMR: *δ*, 40.4 (CH_2), 118.9 (3,5-PyC), 126.4, 127.5, 128.8, 129.4, 129.9, 132.7, 135.1, and 135.6 (PhC), 148.7 (4-PyC), 157.8 (2,6-PyC). MALDI-TOF MS *m/z*: 432 $[M+H]^+$, calcd for $C_{25}H_{22}NS_3$: 432.6.

4.1.13. *tert*-BuS-G2 (15). This compound was prepared analogously to **13** by reacting **14** (1.00 g, 2.32 mmol), K_2CO_3 (396 mg, 2.87 mmol) and **12** (577 mg, 1.10 mmol) in dry DMF (15 mL), except the reaction mixture was stirred at room temperature over a period of 4 h instead of 2 h. After workup, the crude product was purified by flash chromatography on silica gel eluting with 2.5–5% ethyl acetate in CH_2Cl_2 to give **15** as a pale yellow glassy solid (987 mg, 79%). IR (KBr) *ν*: 1601 cm^{-1}. ^1H NMR: *δ*, 1.32 (s, 9H, *t*-Bu), 4.27 (s, 8H, CH_2), 4.36 (s, 4H, CH_2), 7.17 (tt, 4H, *J*=7.2, 1.3 Hz, CH_2S-Ph*H*), 7.24 (tt, 8H, *J*=7.5, 1.4 Hz, CH_2S-Ph*H*), 7.33–7.48 (m, 18H, 2,6-PhH and CH_2S-Ph*H*), 7.29 (s, 4H, Py′H), 7.46 (s, 2H, PyH), 7.59 (d, 2H, *J*=8.3 Hz, 3,5-PhH). ^{13}C NMR: *δ*, 30.9 (C(*C*H_3)$_3$), 39.9 (CH_2), 40.4 (CH_2), 46.3 (*C*(CH_3)$_3$), 118.9 (3,5-Py′C), 119.4 (3,5-PyC), 126.3, 126.9, 127.3, 128.8, 129.2, 129.7, 134.4, 135.6, 135.7, 137.6, 137.8, and 137.9 (PhC), 148.6 (4-Py′C), 149.1 (4-PyC), 157.6 (2,6-PyC), 157.8 (2,6-Py′C). MALDI-TOF MS *m/z*: 1132. $[M+H]^+$, calcd for $C_{67}H_{60}N_3S_7$: 1131.7.

4.1.14. HS-G2 (16). This compound was prepared

analogously to **14** starting from **15** (2.00 g, 1.77 mmol) and purified by repeated precipitation from CH_2Cl_2/hexane to give **16** as a yellow glassy solid (1.85 g, 97%). IR (KBr) ν: 1607 cm^{-1}. ^1H NMR: δ 3.55 (s, 1H, SH), 4.28 (s, 8H, CH_2), 4.34 (s, 4H, CH_2), 7.15–7.45 (m, 38H, PyH, Py′H, PhH and CH_2S-Ph*H*). ^{13}C NMR: δ, 39.9 (CH_2), 40.4 (CH_2), 118.9 (3,5-Py′C), 119.0 (3,5-PyC), 126.3, 127.3, 127.4, 128.8, 129.4, 129.5, 135.5, 135.6, 135.7, 136.6, 137.6, and 138.1 (PhC), 148.7 (4-Py′C), 148.9 (4-PyC), 157.5 (2,6-PyC), 157.7 (2,6-Py′C). MALDI-TOF MS *m/z*: 1075 $[M+H]^+$, calcd for $C_{63}H_{52}N_3S_7$: 1075.6.

4.1.15. *tert*-BuS-G3 (17). This compound was prepared analogously to **13** by reacting **16** (2.00 g, 1.86 mmol), K_2CO_3 (311 mg, 2.25 mmol) and **12** (453 mg, 0.866 mmol) in dry DMF (25 mL), except the reaction mixture was stirred at room temperature for 18 h instead of 2 h. After workup, the crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/EtOAc/NEt_3 9:1:0.5 to give **17** as a pale yellow glassy solid (1.27 g, 61%). IR (KBr) ν: 1602 cm^{-1}. ^1H NMR: δ, 1.31 (s, 9H, *t*-Bu), 4.26 (s, 16H, CH_2), 4.30 (s, 8H, CH_2), 4.33 (s, 4H, CH_2) 7.15 (tt, 8H, $J=7.0$, 1.4 Hz, CH_2S-Ph*H*), 7.22 (tt, 16H, $J=7.6$, 1.3 Hz, CH_2S-Ph*H*), 7.27–7.60 (m, 58H, PyH, Py′H, Py″H, PhH and CH_2S-Ph*H*). ^{13}C NMR: δ, 31.0 (C(*C*H_3)$_3$), 39.8 (CH_2), 39.9 (CH_2), 40.5 (CH_2), 46.4 (*C*(CH_3)$_3$), 118.9 (3,5-Py″C), 119.1 (3,5-Py′C), 119.4 (3,5-PyC), 126.4, 126.9, 127.3, 127.4, 128.9, 129.1, 129.2, 129.3, 129.8, 134.5, 135.3, 135.6, 135.8, 137.7, 137.8, and 138.1 (PhC), 148.6 (4-Py″C), 149.0 (4-Py′C), 149.2 (4-PyC), 157.5 (2,6-PyC), 157.6 (2,6-Py′C), 157.8 (2,6-Py″C). MALDI-TOF MS *m/z*: 2418 $[M+H]^+$, calcd for $C_{143}H_{120}N_7S_{15}$: 2417.5.

4.1.16. HS-G3 (18). This compound was prepared analogously to **14** starting from **17** (1.27 g, 0.525 mmol) and purified by repeated precipitation from CH_2Cl_2/hexane to give **18** as a yellow glassy solid (1.18 g, 92%).

IR (KBr) ν: 1603 cm^{-1}. ^1H NMR: δ 3.52 (s, 1H, SH), 4.25 (s, 16H, CH_2), 4.30 (s, 8H, CH_2), 4.34 (s, 4H, CH_2) 7.12–7.38 (m, 82H, PyH, Py′H, Py″H, PhH and CH_2S-Ph*H*). ^{13}C NMR: δ 39.7 (CH_2), 39.8 (CH_2), 40.4 (CH_2), 118.9 (3,5-Py″C), 119.0 (3,5-Py′C), 119.1 (3,5-PyC), 126.3, 127.3, 127.5, 127.6, 128.8, 128.9, 129.1, 129.2, 129.7, 134.9, 135.1, 135.5, 135.7, 137.6, 137.9, and 138.0 (PhC), 148.6 (4-Py″C), 148.8 (4-Py′C), 149.0 (4-PyC), 157.4 (2,6-PyC), 157.5 (2,6-Py′C), 157.8 (2,6-Py″C). MALDI-TOF MS *m/z*: 2362 $[M+H]^+$, calcd for $C_{139}H_{112}N_7S_{15}$: 2361.4.

4.1.17. $[Fe_2(CO)_6]$-[S-G1]$_2$ (19). To a stirred solution of $Fe_3(CO)_{12}$ (1.17 g, 2.32 mmol) and **14** (1.00 g, 2.32 mmol) in dry THF (30 mL) was added triethylamine (235 mg, 2.32 mmol) and, after 30 min, $HgCl_2$ (629 mg, 2.32 mmol). The resulting mixture was stirred under argon for 14 h, filtered through celite, and washed with CH_2Cl_2 (100 mL). After the solvent was removed, the residue was purified by flash chromatography on silica gel eluted with $CHCl_3$ to give **19** as a red glassy solid (980 mg, 74%). IR (KBr) ν: 2073, 2035, 1996, 1598 cm^{-1}. ^1H NMR: δ, 4.30 (s, 8H, CH_2), 7.15 (t, 4H, $J=6.9$ Hz, CH_2S-Ph*H*), 7.26 (t, 8H, $J=$ 7.5 Hz, CH_2S-Ph*H*), 7.39 (d, 8H, $J=7.1$ Hz, CH_2S-Ph*H*), 7.51 (s, 4H, Py), 7.50–7.52 (m, 8H, PhH). ^{13}C NMR: δ 40.0 (CH_2), 119.1 (3,5-PyC), 126.4, 127.2, 129.2, 129.5, 129.6, 133.1, 136.7, and 137.8 (PhC), 148.2 (4-PyC), 158.8 (2,6-PyC), 208.7 (CO). Anal. calcd for $C_{56}H_{40}Fe_2N_2O_6S_6$ (1141.01): C, 58.95; H, 3.53; N, 2.46. Found: C, 58.30; H, 3.58; N, 2.50.

4.1.18. $[Fe_2(CO)_6]$-[S-G2]$_2$ (20). This compound was prepared analogously to **19** starting from **16** (1.00 g, 0.931 mmol) and purified by flash chromatography on silica gel eluted with 7.5–10% ethyl acetate in CH_2Cl_2 to give **20** as a red glassy solid (778 mg, 69%). IR (KBr) ν: 2073, 2037, 1996, 1601 cm^{-1}. ^1H NMR: δ, 4.25 (s, 16H, CH_2), 4.32 (s, 8H, CH_2), 7.12–7.41 (m, 76H, PyH, Py′H, PhH and CH_2S-Ph*H*). ^{13}C NMR: δ, 39.8 (CH_2), 40.5 (CH_2), 118.9 (3,5-Py′C), 119.1 (3,5-PyC), 126.3, 126.6, 126.8, 127.3, 128.8, 129.0, 129.7, 132.5, 134.5, 135.5, 135.7, and 137.6 (PhC), 148.4 (4-Py′C), 148.6 (4-PyC), 157.7 (2,6-PyC), 157.8 (2,6-Py′C), 207.9 (CO). Anal. calcd for $C_{132}H_{100}Fe_2N_6O_6S_{14}$ (2426.86): C, 65.33; H, 4.15; N, 3.46. Found: C, 64.86; H, 3.94; N, 3.57.

4.1.19. $[Fe_2(CO)_6]$-[S-G3]$_2$ (21). This compound was prepared analogously to **19** starting from **18** (1.00 g, 0.423 mmol) and purified by flash chromatography on silica gel eluted with 5% ethyl acetate in $CHCl_3$ to give **21** as a pale red glassy solid (520 mg, 49%). IR (KBr) ν: 2073, 2036, 1995, 1599 cm^{-1}. ^1H NMR (DMSO-d6, 50 °C): 4.25 (bs, 32H, CH_2), 4.26 (bs, 16H, CH_2), 4.32 (bs, 8H, CH_2), 7.10 (bt, 16H, $J=7.2$, CH_2S-Ph*H*), 7.20 (bt, 32H, $J=7.2$, CH_2S-Ph*H*), 7.29–7.47 (m, 116H, PyH, Py′H, Py″H, PhH and CH_2S-Ph*H*). ^{13}C NMR: δ, 39.7 (CH_2), 39.9 (CH_2), 40.5 (CH_2), 118.9 (3,5-Py″C), 119.0 (3,5-Py′C), 119.2 (3,5-PyC), 126.3, 126.7, 126.9, 127.3, 128.8, 129.2, 129.7, 134.5, 135.1, 135.5, 135.7, 137.6, 138.0, and 138.1 (PhC), 148.6 (4-Py″C), 148.8 (4-Py′C), 149.0 (4-PyC), 157.3 (2,6-PyC), 157.5 (2,6-Py′C), 157.8 (2,6-Py″C) 207.8 (CO). Anal. calcd for $C_{284}H_{220}Fe_2N_{14}O_6S_{30}$ (4998.55): C, 68.24; H, 4.44; N, 3.92. Found: C, 68.18; H, 4.25; N, 3.71.

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References and notes

1. (a) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181–190. (b) Yeung, L. K.; Crooks, R. M. *Nano Lett.* **2001**, *1*, 14–17. (c) Niu, Y.; Yeung, L. K.; Crooks, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 6840–6846. (d) Scott, R. W. J.; Datye, A. K.; Crooks, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 3708–3709. (e) Rahim, E. H.; Kamounah, F. S.; Frederiksen, J.; Christensen, J. B. *Nano Lett.* **2001**, *1*, 499–501. (f) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Nano Lett.* **2002**, *2*, 999–1002. (g) Chung, Y.-M.; Rhee, H.-K. *J. Mol. Catal., A: Chem.* **2003**, *206*, 291–298.
2. (a) Daniel, M.-C.; Ruiz, J.; Nlate, S.; Palumbo, J.; Blais, J.-C.; Astruc, D. *Chem. Commun.* **2001**, 2000–2001. (b) Daniel,

M.-C.; Ruiz, J.; Nlate, S.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **2003**, *125*, 2617–2628.
3. (a) Wang, Y. A.; Li, J. J.; Chen, H.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2293–2298. (b) Zheng, J.; Dickson, R. M. *J. Am. Chem. Soc* **2002**, *124*, 13982–13983. (c) Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 7780–7781.
4. Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.; Jackson, C. L.; Amis, E. J. *Macromolecules* **2000**, *33*, 6042–6050.
5. (a) Zhao, M.; Crooks, R. M. *Chem. Mater.* **1999**, *11*, 3379–3385. (b) Scott, R. W. J.; Ye, H.; Henriquez, R. R.; Crooks, R. M. *Chem. Mater.* **2003**, *15*, 3873–3878. (c) Kim, Y.-G.; Oh, S.-K.; Crooks, R. M. *Chem. Mater.* **2004**, *16*, 167–172.
6. Esumi, K. K.; Nakamura, R.; Suzuki, A.; Torigoe, K. *Langmuir* **2000**, *16*, 7842–7846.
7. Michels, J. J.; Huskens, J.; Reinhoudt, D. N. *J. Chem. Soc., Perkin Trans. 2* **2002**, 102–105.
8. (a) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877–4878. (b) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355–7356.
9. Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.
10. Kim, M.-K.; Jeon, Y.-M.; Jeon, W. S.; Kim, H.-J.; Hong, S. G.; Park, C. G.; Kim, K. *Chem. Commun.* **2001**, 667–668.
11. Wang, R.; Yang, J.; Zheng, Z.; Carducci, M. D.; Jao, J.; Seraphin, S. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 549–552.
12. Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141–1142.
13. (a) Gorman, C. B.; Smith, J. C. *Acc. Chem. Res.* **2001**, *34*, 60–71. (b) Chasse, T. L.; Yohannan, J. C.; Kim, N.; Li, Q.; Li, Z.; Gorman, C. B. *Tetrahedron* **2003**, *59*, 3853–3861. (c) Chasse, T. L.; Sachdeva, R.; Li, Q.; Li, Z.; Petrie, R. J.; Gorman, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 8250–8254. (d) Gorman, C. B. *C. R. Chimie* **2003**, *6*, 911–918.
14. (a) Chessa, G.; Canovese, L.; Visentin, F.; Uguagliati, P. *Inorg. Chem. Commun.* **1999**, *2*, 607–608. (b) Chessa, G.; Canovese, L.; Gemelli, L.; Visentin, F.; Seraglia, R. *Tetrahedron* **2001**, *57*, 8875–8882. (c) Canovese, L.; Chessa, G.; Visentin, F.; Uguagliati, P. *Coord. Chem. Rev.* **2004**, *248*, 945–954.
15. Delgado, E.; Hernández, E.; Mansilla, N.; Zamora, F.; Martínez-Cruz, L. A. *Inorg. Chim. Acta* **1999**, *284*, 14–19.
16. (a) Markees, D. G.; Kidder, G. W. *J. Org. Chem.* **1956**, *78*, 4130–4135. (b) Bhattacharya, S.; Snehalatha, K.; George, S. K. *J. Org. Chem.* **1998**, *63*, 27–35.
17. Lüning, U.; Baumstark, R.; Müller, M. *Liebigs Ann. Chem.* **1991**, 987–998.
18. Bolletta, F.; Garelli, A.; Montalti, M.; Prodi, L.; Romano, S.; Zaccheroni, N.; Canovese, L.; Chessa, G.; Santo, C.; Visentin, F. *Inorg. Chim. Acta* **2004**, *357*, 4078–4084.
19. Lennox, J. R.; Turner, S. C.; Rapoport, H. *J. Org. Chem.* **2001**, *66*, 7078–7083.
20. Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095–6097.
21. Lohose, O.; Thevenin, P.; Waldvogel, E. *Synlett* **1999**, 45–48.
22. Kelly, S.; Foricher, Y.; Mann, J.; Bentley, J. M. *Org. Biomol. Chem.* **2003**, *16*, 2865–2876.
23. (a) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991; pp 277–297. (b) Hsung, R. P.; Babcock, J. R.; Chidsey, C. E. D.; Sita, L. R. *Tetrahedon Lett.* **1995**, *36*, 4525–4528.
24. (a) Kiso, Y.; Nakamura, S.; Ito, K.; Ukawa, K.; Kitagawa, K.; Akita, T.; Moritoki, H. *J. Chem. Soc. Commun.* **1979**, 971–972. (b) Barlaam, B.; Bird, T. G.; Lambert-van der Brempt, C.; Cambell, D.; Foster, S. J.; Maciewicz, R. *J. Med. Chem.* **1999**, *42*, 4890–4908.
25. Seyfert, D.; Archer, C. M.; Ruschke, D. P. *Organometallics* **1991**, *10*, 3363–3380.